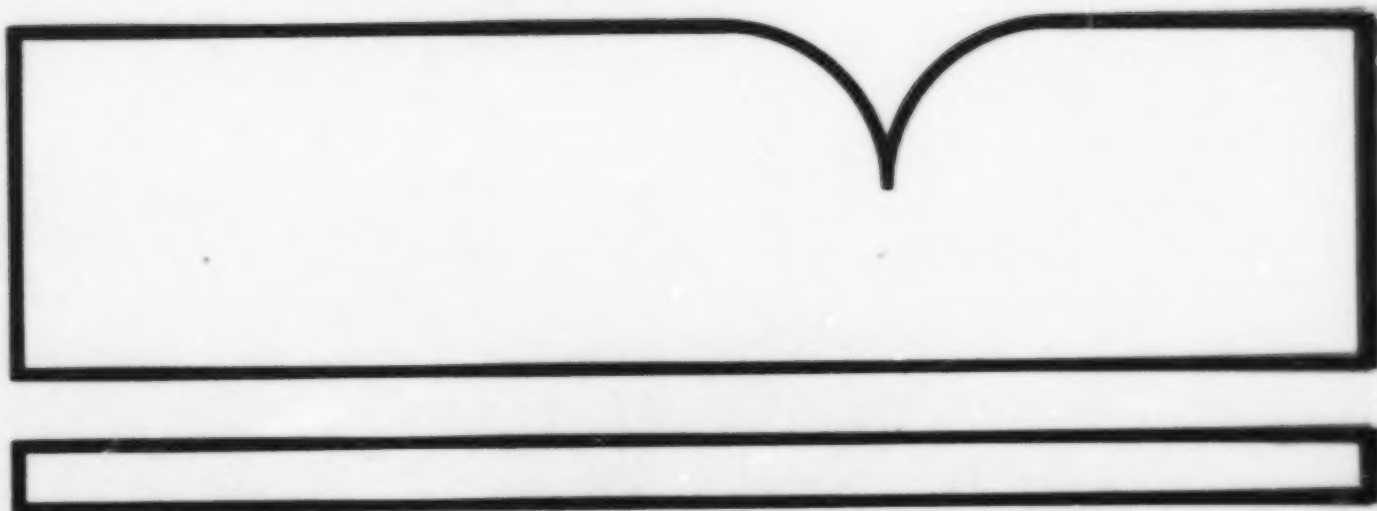


Organics in the Environment

(U.S.) Environmental Monitoring and Support Lab.
Cincinnati, OH

May 79



U.S. Department of Commerce
National Technical Information Service

NTIS.

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA-600/J-79-117	2. JOURNAL ARTICLE	3. RECIPIENT'S ACCESSION NO. PBI 148744
4. TITLE AND SUBTITLE ORGANICS IN THE ENVIRONMENT		5. REPORT DATE May 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) William L. Budde and James W. Eichelberger		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring and Support Lab., Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as Above		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA-600/06
15. SUPPLEMENTARY NOTES Published in Analytical Chemistry, May 1979 by American Chemical Society		
16. ABSTRACT With the large number of measurement techniques available, the designer of an environmental monitoring system must select those most appropriate for the situation. Although many tools exist, each has a different capability, cost, and complexity of operation.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

Organics

in the Environment

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In the United States the period beginning about 1970 will likely be described by legal historians as the great era of environmental law. Among the many recent pieces of Federal legislation dealing with the environment, several address in some detail the problem of pollution by toxic and potentially carcinogenic organic compounds. Major legislation in this category includes the 1972 amendments to the Federal Water Pollution Control Act (PL 92-500), the Safe Drinking Water Act of 1974 (PL 93-523), and the Toxic Substances Control Act of 1976 (PL 94-469). Among other requirements, these laws establish the need for extensive measurements of the presence and concentration of a broad variety of organic compounds in a number of different sample types.

The major thrust behind the passage of the new legislation was the correlations of adverse health or ecological effects with measurements of the presence and concentration of a variety of pollutants. These measurements were made possible by significant advances in analytical instrumentation, electronics, computer science, and analytical chemistry during the 1960's and early 1970's. For the identification and measurement of organic compounds, major breakthroughs included the discovery of gas chromatography; the development of the electron capture, flame ionization, and other detectors; the application of the mass spectrometer as a detector in gas chromatography; the development of

the quadrupole mass spectrometer; and the extensive advances in solid state microelectronics that made possible the relatively low-cost digital computer. Today there is available an array of powerful tools for the measurement of organic pollutants, and the future will undoubtedly provide more. For example, high-performance liquid chromatography is an important new tool in many areas of analytical chemistry, and it should have many significant applications in environmental chemistry. The leaders of the environmental movement and those who are pleased with the general public concern for the environment should not forget the major contributions from analytical chemistry and the developers of new analytical methods. On the other hand, it is ironic that environmental regulation may often impact heavily certain organizations that made significant contributions to the advances in analytical techniques.

Selection of Analytical Methods

With the large number of measurement techniques available, the designer of an environmental monitoring system must select those most appropriate for the situation. Although many tools exist, each has a different capability, cost, and complexity of operation. This section is intended to present general guidelines for the selection of analytical methodology for organic compounds. The discussion will emphasize compounds that are

sufficiently volatile for gas chromatography because these have been studied most during the last 20 years. However, the principles are general and apply to all types of organic compounds.

There are two general goals that affect the method selection process. The target compound (TC) goal is traditional in chemical analysis and is widely accepted in related sciences. The target compounds, whose concentrations are desired, are usually contained on a list submitted to the analytical laboratory. The list of target compounds affects method selection because with this goal, sample processing and measurement methods may be optimized for the target compounds. Detailed chemical-instrumental procedures may be designed to isolate the target compounds from the sample matrix and known interferences, concentrate the target compounds, and measure their concentrations with various general purpose or selective detectors. Laboratory control standards are usually employed to establish that isolation does occur, and to optimize the procedure for maximum recovery of the desired components and minimum interference from other components. Chromatographic separations are included in the optimization process.

The gas chromatography-electron capture detector procedures for chlorinated hydrocarbon pesticides are examples of the optimized target compound approach. However, the justifi-

cation for selection of a specific method requires more information than the decision to measure target compounds. The additional information needed is discussed after a presentation of the other general type of analytical goal.

The broad spectrum (BS) approach is in sharp contrast to the TC approach. The idea of the BS approach is to seek a broad spectrum picture of whatever is present in a sample as a major or minor component. This kind of analysis is not guided by a predetermined list of compounds to be measured. The BS approach has existed since the beginning of chemical analysis. However, the practical and economic pursuit of this goal was often not possible in the past. The development of the computerized gas chromatography-mass spectrometry system, and other similar technologies, has made this goal a feasible and desirable alternative for many types of samples.

With the BS approach, sample preparation is designed to be as simple as possible to preclude losses of significant sample components and to minimize the possibility of sample contamination. The idea is to divide the sample into broad classes of compounds and to apply general purpose chromatographic methods for the separation of the compounds in each group. Literally hundreds of thousands of compounds can be potentially included in a broad class, but it is usually safe to assume that only a relatively few compounds are present in each class in most samples.

For the BS approach a spectroscopic detector is required. Spectroscopic detectors are defined as devices that continuously measure spectra of energy absorptions, ion abundances, etc., of various components as they elute from a chromatographic system. The spectra are of sufficient quality to permit identification of components without prior knowledge of which compounds are present. A gas chromatography-mass spectrometry (GC/MS) system operating in the continuous repetitive measurement of spectra mode is a spectroscopic detector, but a GC/MS system operating in the selected ion monitoring mode of data acquisition (1) is not. The very nature of the BS approach implies the need to generate information sufficient to recognize and identify the unexpected. The most beneficial result of the BS approach is the frequent discovery of significant but previously unrecognized pollutants.

If the decision is made to use the BS approach, method selection is restricted. Gas chromatography-mass spectrometry may be the only viable choice, although additional tools should become available in the future.

On the other hand, if the decision is made to use the TC approach, careful consideration of the sample type is necessary before a method selection can be made. Environmental systems may be divided into three broad classes:

1. Systems of type 1 are relatively closed, i.e., there is some control of the entry of components into the system, and all components are well defined. An example is the output from a chemical plant that uses raw materials of known composition, processes them according to a particular procedure, and generates products and by-products that are well-defined.

2. Systems of type 2 are somewhat open in that entry of new components is possible but not frequent or likely, and the components are somewhat defined. An example is the output from a drinking water treatment plant that uses an uncontaminated ground water source, and chlorinates to produce a more or less constant variety of halogenated methanes.

3. Systems of type 3 are wide open to entry of almost anything at any time, and components are poorly defined. An example is the Mississippi River at St. Louis, Mo.

For measurements with a type 1 environmental system and a TC analytical goal, reliable results may be obtained with a chromatographic method and a conventional general purpose or selective detector, e.g., flame ionization or electron capture. With this type of sample the probability of unexpected components is low. The optimized TC procedures assure that most or all potential interferences are eliminated and, if a selective detector is used, the effects of interfering substances are reduced further. Under these conditions the retention index may be a reliable method of peak identification. The often-cited advantage of this approach is the potential economy of operation since the equipment employed is relatively simple, inexpensive, and easy to use by relatively low-cost technicians. The principal disadvantage is that in order to include all environmentally significant compounds, literally hundreds of different procedures need to be developed, tested, and documented. The implementation of all these procedures for a defined but relatively complex sample would be slow, complex, and relatively costly.

With type 2 environmental systems and a TC goal, the probability of unexpected components increases. If these unexpected components are interferences that are not eliminated by the sample preparation, there is a clear possibility of erroneous results if a general purpose chromatographic detector is in use. For type 2 environ-

mental systems a selective chromatographic detector or a spectroscopic detector is required. Microcoulometric, electrolytic conductivity, or flame photometric gas chromatographic detectors are selective and may be appropriate choices. A gas chromatography-mass spectrometry system operating in the selected ion monitoring mode of data acquisition (1) is a highly selective detector. However, for measurements of type 2 systems, it is recommended that a spectroscopic detector be used regularly to confirm a fixed percentage of the identifications and to analyze any samples that deviate from the normal pattern.

With a type 3 environmental system and a TC goal, the application of a spectroscopic detector is required. With the type 3 system the probability of unexpected compounds is high, and the qualitative information produced by conventional chromatography detectors is insufficient for reliable identifications. Again, as in the BS approach, the only viable tool may be gas chromatography-mass spectrometry (GC/MS). General purpose conventional chromatography detectors may have several important applications in support of the GC/MS methodology. These include prescreening to determine dilution requirements, to eliminate samples with no components above a given threshold, or to optimize chromatography operating parameters.

Cost Considerations

Many decisions of method selection are greatly influenced by cost considerations. If cost considerations are used, the total cost of an analytical method should be used. This should include the following:

- Equipment investment
- Sample preparation costs
- Instrumentation operating costs
- Quality control costs
- Equipment maintenance costs
- Training and management costs

There is some indication that for measurements of relatively large numbers of target compounds, e.g., 40-60 or more, in type 1 or 2 environmental samples, broad spectrum type methods may be less costly per TC than chromatography methods that use conventional general purpose or selective detectors and optimized sample preparation procedures. Figure 1 shows plots of changing approximate (indicated by the broad bands) total costs as a function of the number of target compounds for a mass spectrometer and conventional detectors. With a small number of target compounds, total costs are dominated by equipment capital costs, and the mass spectrometer approach is relatively

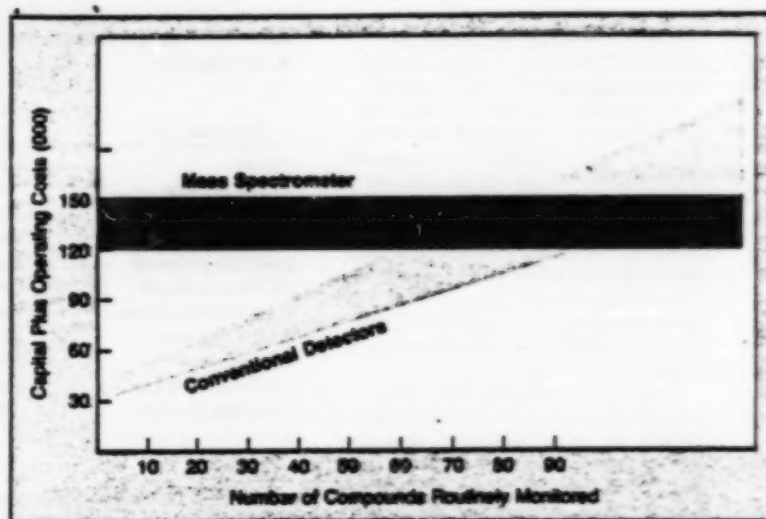


Figure 1. Capital plus operating costs for mass spectrometer and conventional detectors as a function of the number of compounds routinely monitored

expensive. However, as the number of target compounds increases, the cost of the GC/MS approach remains relatively constant, while the costs of methods using conventional detectors increase significantly. There appear to be three general reasons for this trend:

Optimized TC sample preparation procedures are often quite rigorous and complex to assure that most or all potential interferences are eliminated, and these kinds of procedures must be employed with conventional chromatography detectors. With a mass spectrometer the sample preparation may often be much simpler, analogous to the BS approach, because the mass spectrometer output provides adequate information, in most cases, to reliably identify most components of the sample.

For a broad range of target compounds, a variety of conventional chromatography detectors and supporting equipment is required. This is because chromatography detectors are designed for some selectivity to further minimize the effects of interfering substances. As the number of target compounds increases so does their diversity, hence, the need for more equipment. On the other hand, the mass spectrometer is a universal detector which precludes interference by the very nature of its output. It can accommodate a variety of compound types without a significant change in operating procedures.

Conventional chromatography methods with general purpose or selective detectors often rely heavily on retention indices for the identification of compounds. This requires the rigorous control of operating conditions that could affect the retention index.

e.g., flow rates, temperatures, temperature programming rates, etc. Measurements of control standards must be made at frequent intervals to assure that conditions are well controlled. With a GC/MS retention indices are not critical and careful control of operating conditions that affect them is not critical.

For monitoring a large number of target compounds encompassing a broad range of compound types, it appears that the additional cost of

GC/MS instrumentation is offset by savings in other equipment and operating costs. Additional experience with all the methods discussed over the next few years will permit more exact quantitation of the cost-effectiveness of various approaches.

Priority Pollutant Program

The U.S. Environmental Protection Agency's (EPA) priority pollutant program is an example of the application of the method selection guidelines. During 1976 the EPA was required to begin a program to establish industrial wastewater effluent limitations for a group of 129 priority pollutants, and to recommend treatment technology to meet the limitations. The priority pollutants were selected on the basis of known human or animal toxic and carcinogenic effects. The 129 materials included 106 specific organic compounds, nine product formulations that are mixtures of organic compounds, twelve metals, cyanide ion, and asbestos. The first step in the process of establishing limitations was a major program to identify and measure these materials in various wastewaters from a number of industries.

Clearly, the analytical goal of the organics analysis was a group of target compounds, and the samples were of type 3, i.e., uncharacterized with poorly defined components. Also a rather large number of target com-

Table I. The 46 Compounds of the Base-Neutral Fraction

Compound name	CAS Registry Number	Compound name	CAS Registry Number
1,3-Dichlorobenzene	541-73-1	Diethylphthalate	84-86-2
1,4-Dichlorobenzene	106-48-7	N-Nitrosodiphenylamine	86-30-6
1,2-Dichlorobenzene	95-50-1	Hexachlorobenzene	118-74-1
Hexachloroethane	67-72-1	4-Bromophenyl phenyl ether	101-55-3
bis(2-Chloroethyl)ether	111-44-4	Phenanthrene	85-01-8
bis(2-Chloroisopropyl)ether	39638-32-9	Anthracene	120-12-7
N-Nitrosodi-n-propylamine	821-64-7	Di-n-butylphthalate	84-74-2
Isophorone	78-59-1	Fluoranthene	106-44-0
Nitrobenzene	98-59-1	Pyrene	129-00-0
Hexachlorobutadiene	87-68-3	Benzidine	98-87-5
1,2,4-Trichlorobenzene	129-82-1	Butylbenzylphthalate	85-88-7
Naphthalene	91-10-3	bis(2-Ethylhexyl)phthalate	117-81-7
bis(2-Chloroethoxy)methane	111-91-1	Chrysene	218-01-9
Hexachlorocyclopentadiene	77-47-4	Benzo(a)anthracene	56-55-3
2-Chloronaphthalene	91-58-7	Benzo(b)fluoranthene	205-99-2
Acenaphthylene	208-96-8	Benzo(k)fluoranthene	207-08-9
2,6-Dinitrotoluene	806-20-2	3,3'-Dichlorobenzidine	91-94-1
Acenaphthene	83-32-9	Di-n-octylphthalate	117-84-0
Dimethylphthalate	131-11-3	Benzo(a)pyrene	50-32-8
Fluorene	86-73-7	Indeno(1,2,3-cd)pyrene	193-39-5
4-Chlorophenyl phenyl ether	7005-72-3	Dibenzo(a,h)anthracene	53-70-3
2,4-Dinitrotoluene	121-14-2	Benzo(g,h,i)perylene	191-24-2
1,2-Diphenylhydrazine	122-66-7	Nitrosodimethylamine	62-75-9

pounds was of interest, and these covered a range of chemical and physical properties. All of these factors pointed to the selection of broad spectrum sample preparation methods, extensive use of gas chromatography, and a spectroscopic detector. Gas chromatography-mass spectrometry was selected as the basis for the analytical protocol. The target compounds were divided into five broad classes as follows:

A group of 46 compounds isolated from a pH = 11 adjusted sample by extraction with methylene chloride. These compounds are identified and measured by GC/MS and are listed in Table I.

A group of 26 compounds and product formulations extracted from a sample at ambient pH with 15% methylene chloride in hexane. These compounds are shown in Table II. They are initially detected by gas chromatography with an electron capture de-

tector, but must be confirmed by GC/MS. There may be some overlap between this and the first fraction.

A group of 30 compounds isolated by the inert gas purge and trap procedure (2), and identified and measured with GC/MS. These compounds are shown in Table III, and there may be some overlap with the other fractions.

A group of 11 compounds extracted from a sample adjusted to pH = 2. The solvent is methylene chloride and these compounds are shown in Table IV. The identification and measurement is by GC/MS.

Finally, two compounds, acrolein and acrylonitrile, are very water soluble and not easily isolated from aqueous samples. These are identified and measured by direct aqueous injection GC/MS (3). These are also shown in Table III.

In addition to the compound names, Tables I-IV show the Chemical Abstract Service (CAS) Registry num-

Table IV. The 11 Compounds of the Acid Fraction

Compound name	CAS Registry Number
Phenol	108-95-2
2-Chlorophenol	95-67-8
2-Nitrophenol	88-75-5
2,4-Dimethylphenol	105-67-9
2,4-Dichlorophenol	120-83-2
p-Chloro-m-cresol	59-50-7
2,4,6-Trichlorophenol	88-06-2
2,4-Dinitrophenol	51-28-5
4-Nitrophenol	100-02-7
4,6-Dinitro-o-cresol	534-52-1
Pentachlorophenol	87-86-5

bers. These unique identifiers are useful for computer storage and retrieval of results, and searching of related data bases for information about a particular substance. The quantitative analysis by GC/MS includes an extensive quality control program to establish the precision and accuracy of the measurements in a variety of concentration ranges. A great deal of information about the precision and accuracy of these measurements should become available in the next few years.

Acknowledgment

The authors thank Robert Kleopfer, EPA, who provided the CAS Registry numbers and other information about the priority pollutant list.

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- (3) L. E. Harris, W. L. Budde, and J. W. Eichelberger, *Anal. Chem.*, 46, 1912 (1974).

Table II. The 26 Compounds of the Pesticide Fraction

Compound name	CAS Registry Number	Compound name	CAS Registry Number
β -Endosulfan	33213-65-9	Endosulfane sulfate	1031-07-8
α -Benzenehexachloride	319-84-8	δ -Benzenehexachloride	319-86-3
γ -Benzenehexachloride	58-99-8	Chlordane	57-74-9
β -Benzenehexachloride	319-85-7	Toxaphene	8001-35-2
Aldrin	309-00-2	Aroclor-1242	53489-21-9
Heptachlor	76-44-8	Aroclor-1254	11097-89-1
Heptachlor epoxide	1024-57-3	Aroclor-1221	11104-28-2
δ -Endosulfan	959-98-8	Aroclor-1232	11141-16-5
Dieldrin	30-57-1	Aroclor-1248	12672-29-6
4,4'-DDE	72-55-9	Aroclor-1260	11098-82-5
4,4'-DDD	72-54-8	Aroclor-1016	12674-11-2
4,4'-DDT	50-28-3	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6
Endrin	72-20-8	Endrin aldehyde	

Table III. The 30 Compounds of the Purgable Fraction and Two Direct Aqueous Analytes

Compound name	CAS Registry Number	Compound name	CAS Registry Number
Acrolein	107-02-8	Bromodichloromethane	75-27-4
Acrylonitrile	107-13-1	bis(Chloromethyl)ether	542-88-1
Chloromethane	74-87-3	1,2-Dichloropropane	78-87-5
Dichlorodifluoromethane	75-71-8	Benzene	71-43-2
Bromomethane	74-83-9	trans-1,3-Dichloropropene	542-75-6
Vinyl chloride	75-01-4	cis-1,3-Dichloropropene	542-75-6
Chloroethane	75-00-3	Trichloroethylene	79-01-6
Methylene chloride	75-08-2	Dibromochloromethane	124-48-1
Trichlorofluoromethane	75-69-4	1,1,2-Trichloroethane	79-00-5
1,1-Dichloroethylene	75-35-4	2-Chloroethyl vinyl ether	110-75-8
1,1-Dichloroethane	75-34-3	Bromoform	75-25-2
trans-1,2-Dichloroethylene	540-59-0	1,1,2,2-Tetrachloroethane	127-18-4
Chloroform	67-66-3	Toluene	108-88-3
1,2-Dichloroethane	107-06-2	1,1,2,2-Tetrachloroethane	79-34-5
1,1,1-Trichloroethane	71-55-6	Chlorobenzene	108-90-7
Carbon tetrachloride	56-23-5	Ethyl benzene	100-41-4



William L. Budde (left) and James W. Eichelberger, both of the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, are actively engaged in the development of GC/MS methods for the determination of organic pollutants.